(12) UK Patent Application (19) GB (11) 2 246 741 (13) A

(43) Date of A publication 12.02.1992

(21) Application No 9111279.7

(22) Date of filing 24.05.1991

(30) Priority data
(31) 529067 (32) 25.05.1990 (33) US

(71) Applicant
W R Grace & Co - Conn

(Incorporated in the USA - Connecticut)

Grace Plaza, 1114 Avenue of the Americas, New York, N.Y.10036, United States of America

(72) Inventor
Gautam P Shah

(74) Agent and/or Address for Service
J A Kemp & Co
14 South Square, Gray's Inn, London, WC1R 5LX, United Kingdom

(51) INT CL[5]
B32B 27/08 27/30 27/32

(52) UK CL (Edition K)
B5N N195 N196 N207 N21Y N223 N255 N257 N259 N260 N261 N262 N266 N267 N2704 N2708 N273 N2730 N2732 N277 N281 N291 N293 N353 N37X N372 N434 N437 N46X N460 N469 N48X N491 N496 N510 N518 N57Y N58X N58Y N591 N595 N599 N60Y N603 N611 N62X N62Y N648 N650 N658 N66Y N661 N670 N677 N680 N70X N705 N707 N735 N738 N78X
U1S S1814 S3028

(56) Documents cited
US 4572854 A

(58) Field of search
UK CL (Edition K) B5N
INT CL[5] B32B
Online databases: WPI

(54) **Food packaging film**

(57) A polymeric film comprises a core layer of ethylene-vinyl alcohol copolymer, and two outer layers of ethylene propylene terpolymer. The outer layers are preferably blended with polypropylene. A preferred embodiment of the multilayer film, if coextruded, also includes intermediate polymeric adhesive layers. This film exhibits excellent optical properties and shrink properties while providing high oxygen barrier and is especially useful in food packaging applications.

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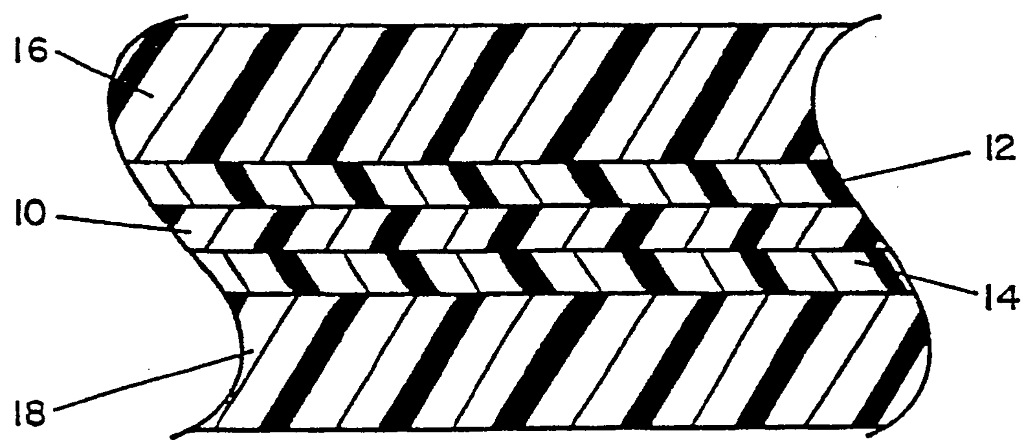

FIG. 1

ETHYLENE PROPYLENE TERPOLYMER FILM

This invention relates to oriented, thermoplastic films for packaging; and more particularly, this invention relates to a coextruded multilayer, oriented film having high oxygen barrier characteristics.

Thermoplastic film, and in particular polyolefin materials, have been used for some time in connection with packaging of various articles including food products which require protection from the environment, an attractive appearance, and resistance to abuse during the storage and distribution cycle. Suitable optical properties are also desirable in order to provide for inspection of the packaged product after packaging, in the distribution chain, and ultimately at point of sale. Optical properties such as high gloss, high clarity, and low haze characteristics contribute to an aesthetically attractive packaging material and packaged product to enhance the consumer appeal of the product. Various polymeric materials have been used to provide lower gas permeability in order to reduce the transmission of oxygen through the packaging film and thereby retard the spoilage and extend the shelf life of products such as food items which are sensitive to oxygen.

It is also often desirable to include in a packaging film a shrink feature, i.e, the propensity of the film upon exposure to heat to shrink or, if restrained, create shrink tension within the packaging film. This property is imparted to the film by orientation of the film during

its manufacture. Typically, the manufactured film is stretched in either a longitudinal (machine) direction, a transverse direction, or both, in varying degrees to impart a certain degree of shrinkability in the film upon subsequent heating. After being so stretched, the film is rapidly cooled to provide this latent shrinkability to the resulting film. One advantage of shrinkable film is the tight, smooth appearance of the wrapped product that results, providing an aesthetic package as well as protecting the packaged product from environmental abuse. Various food and non-food items may be and have been packaged in shrinkable films.

It is sometimes also desirable to orient a packaging film and thereafter heat set the film by bringing the film to a temperature near its orientation temperature. This produces a film with substantially less shrinkability, while retaining much of the advantages of orientation, including improved modulus and optical properties.

Ethylene vinyl alcohol copolymer (EVOH) is known as an oxygen barrier material, and has been used in the past in conjunction with multilayer packaging films.

U.S. Patent No. 4,064,296 issued to Bornstein et al discloses a film formed by the coextrusion of hydrolyzed ethylene vinyl acetate (HEVA) with outside layers of, for example, ethylene vinyl acetate copolymer (EVA).

Also of interest is U.S. Patent No. 4,464,443 issued to Farrell et al showing the use of EVOH in a multilayer polymer structure, and including drying agents or desiccants such as sodium phosphate-di-basic and calcium chloride. EVOH, although a good barrier material, is moisture sensitive, and loses a great deal of its barrier properties at higher levels of relative humidity.

Also of interest is U.S. Patent No. 4,457,960 issued to Newsome which discloses use of EVOH and EVOH blends in a multiple layer film. The film may be made as shrinkable film, and may be melt extruded.

Also of interest is U.S. Patent No. 4,495,249 issued to Ohya et al and disclosing a multilayer laminate film with a core layer of a saponified copolymer of ethylene and vinyl acetate, and including two outer layers of a mixture of copolymer of ethylene and vinyl acetate and a copolymer of propylene and ethylene or linear low density polyethylene. The multilayer laminate film of the reference can be made heat shrinkable and has gas barrier properties.

U. S. Patent No. 4,284,674 (Sheptak) discloses a multilayer film having a core layer of ethylene vinyl alcohol copolymer adhered on each side to nylon, each nylon layer in turn being adhered to a chemically modified polyolefin, and a further layer of primer material suitable to adhere the modified polyolefin to an outer layer of polypropylene or other material suitable for conveying toughness, flex crack resistance, and moisture carrier properties to the multi-ply film.

U. S. Patent No. 4,355,721 issued to Knott et al discloses a coextruded multilayer sheet having a first layer of nylon, an EVOH barrier layer, another layer of nylon, an adhesive layer, and an inside surface layer of, for example, propylene homopolymer or ethylene propylene copolymer.

U. S. Patent No. 4,182,457 (Yamada et al) discloses a container with an EVOH core, adhesive layers, and additional layers of e.g. polypropylene or ethylene propylene copolymer.

U. S. Patent No. 4,511,610 (Yazaki et al) discloses a container with an EVOH core, adhesive layers, and additional layers of e.g. polypropylene or ethylene propylene copolymer.

U. S. Patent No. 4,561,920 (Foster) discloses a film with an EVOH core, adhesive layers, and additional layers of e.g. polypropylene or ethylene propylene copolymer.

U. S. Patent No. 4,405,667 issued to Christensen et al appears to disclose a retortable pouch having a linear low density polyethylene

heat seal layer, a second layer of a blend of linear low density polyethylene and propylene ethylene copolymer, optional third, fourth, and fifth layers of propylene ethylene copolymer, a sixth layer of an anhydride modified polypropylene, a seventh layer of nylon, an eighth layer of EVOH and a ninth layer of nylon.

U. S. Patent No. 4,421,823 issued to Theisen et al appears to disclose a flexible wrapping material of limited construction having a biaxially oriented polypropylene/oxygen barrier substrate, in which the oxygen barrier material may be EVOH; an extrusion laminate of a biaxially oriented polymer such as polypropylene or nylon, bonded to polyethylene; and a layer of heat sealable polymeric material such as ethylene vinyl acetate copolymer laminated to the substrate. A special polymer which may be, for example, polyethylene or ethylene vinyl acetate copolymer is bonded to one surface of the biaxially oriented polypropylene.

U. S. Patent No. 4,532,189 issued to Mueller discloses a shrink film having two skin layers each comprising e.g. a blend of polypropylene and ethylene propylene copolymer.

U. S. Patent No. 4,588,648 issued to Krueger et al discloses a multiple layer plastic film having polypropylene adhered to nylon by an intermediate layer of a blend of an ungrafted propylene-based polymer and a graft copolymer of maleic anhydride onto a olefin polymer or copolymer, with additional layers of nylon, EVOH and nylon.

Also of interest is U.S. Patent No. 4,400,428 issued to Rosenthal et al which discloses a composite film having a biaxially oriented polypropylene based film (BOPP) laminated on at least one surface with a multilayer structure including a gas barrier layer of a hydrolyzed ethylene vinyl acetate copolymer and a layer adjacent to the base film, and a heat sealable outer layer which may be, for example, modified propylene/ethylene copolymer. Adhesion-promoting layers of modified

polyolefin may include polypropylene containing grafted units of alpha, beta-monounsaturated dicarboxylic acids.

U. S. Patent No. 4,501,797 issued to Super et al discloses an unbalanced oriented multiple layer film including a first layer of polypropylene, a second layer of an anhydride modified polypropylene, and a third layer of ethylene vinyl alcohol.

U. S. Patent No. 4,572,854 (Dallmann et al) discloses a multilayer barrier film having a core layer of saponified ethylene vinyl acetate copolymer, intermediate adhesion-promoting layers of modified polyolefin, and an outer layer of polypropylene homopolymer or copolymer.

U. S. Patent No. 4,726,984 (Shah) discloses an oriented film with a core layer of EVOH, adhesive layers, and outer layers of a blend of ethylene propylene copolymer and polypropylene.

U. S. Patent No. 4,828,928 (Shah) discloses a monoaxial shrink film with a core layer of high density polyethylene, outer layers of ethylene propylene copolymer and/or polypropylene, and intermediate bonding layers.

EPO Patent Application No. 175451A discloses a film of ionomer/adhesive/EVOH/adhesive/polypropylene.

EPO Patent Application No. 0,149,321 (Ohya et al) discloses a heat shrinkable tubular film having a gas barrier layer of vinylidene chloride copolymer, outer layers of polyolefin such as ethylene propylene copolymer, polypropylene and mixtures thereof, at least one intermediate layer of for example a polyamide, and adhesive layers disposed between any of the above layers.

U. K. Patent Application GB 2,076,741B (Ferguson et al) discloses a film with a base layer of polypropylene and a skin layer of a blend of polypropylene and propylene-ethylene copolymer.

U. K. Patent Application GB 2,048,209A (Yamada et al) discloses a squeeze vessel with an EVOH core, adhesive layers, and additional layers of e.g. polypropylene and/or ethylene propylene copolymer.

U. K. Patent Application GB 2,139,948A (Dobbie) discloses a multilayer, preferably coextruded five-layer heat sealable film having a surface layer of a heat sealable polymer such as linear low density poluethylene or LLDPE blended with other polymers such as EVA, an EVOH layer, and a layer of polypropylene. These layers can be bonded by polymeric adhesive tie layers.

Barrier Plastics -Circa 1985 by Stanley Sacharow, in Paper Film, & Foil Converter, June 1985, pages 118-122 discloses a bottle of six-ply polypropylene/regrind/tie/EVOH/tie/polypropylene construction.

It is an object of the present invention to provide a coextruded thermoplastic multilayer film characterized by good oxygen barrier properties over a wide range of moisture conditions.

It is a further object of the present invention to provide a thermoplastic multilayer film having an aesthetic appearance with good clarity, and other desirable optical properties.

It is another object of the present invention to provide a thin thermoplastic multilayer film having superior toughness and abrasion resistance.

It is still another object of the present invention to provide a coextruded thermoplastic multilayer film which may be totally coextruded, and oriented to provide a film with good shrink properties and good barrier properties over a wide range of moisture conditions.

It is yet another object of the present invention to provide a coextruded thermoplastic film which is oriented yet substantially shrink-free.

The present invention relates to a polymeric film comprising a core layer comprising ethylene vinyl alcohol copolymer, and two outer layers comprising ethylene propylene terpolymer. Polypropylene is optionally blended with the terpolymer prior to assembling the layers together.

In another aspect of the invention, a method of making a coextruded, thermoplastic multilayer film comprises the steps of coextruding an inner layer of ethylene vinyl alcohol copolymer between two outer layers of an ethylene propylene butene terpolymer and polypropylene to form a multilayer film; and stretching the multilayer film to orient it.

"Intermediate layer" and the like is used herein to define a layer in a multilayer film enclosed on both sides by other layers.

The term "oriented" and the like is used herein to define a polymeric material in which the molecules have been aligned by a process such as racking or blown bubble process.

"Ethylene vinyl alcohol copolymer" and the like as used herein includes saponified or hydrolyzed ethylene vinyl acetate copolymers.

"Ethylene propylene terpolymer" is used herein to mean a terpolymer of ethylene, propylene, and a comonomer such as a diene, butylene, or other suitable comonomers which can be used in film applications.
"Racking" as used herein is a well-known process for stretching coextruded and reheated multilayer film by means of tenter framing or blown bubble processes.

Further details are given below with reference to the sole drawing figure wherein Figure 1 is a schematic cross section of a preferred embodiment of a multilayer film of the invention.

Referring specifically to the drawings, in Figure 1, a schematic cross section of a preferred embodiment of the coextruded multilayer oriented film of the invention is shown. Film structure is directed to a multilayer film having the generalized structure of A/B/C/B/A where A is an outer layer, B is an intermediate adhesive layer, and C is a core layer of a barrier material. Preferably, core layer 10 is ethylene vinyl alcohol copolymer. Intermediate layers 12 and 14 are preferably carboxylic acid or acid anhydride-modified polyolefins and more preferably polypropylene-based carboxylic acid or acid anhydride-modified polyolefins. Outer layers 16 and 18 are preferably a blend of ethylene propylene terpolymer (EPT) and polypropylene (PP). These blend layers may include from 0-100% EPT and 100%-0% PP, although preferably the blend layers include between about 96% and 85% EPT and between about 15% and 4% PP; even more preferably, the blend layer includes about 92% EPT and 8% PP.

The following Examples illustrate the invention.

EXAMPLE 1

Ethylene propylene terpolymer (Moplen EP 3-C 37 F from Himont) was blended with polypropylene (Himont PDO 64). The polypropylene was pre-blended with about 4% by weight of a silica-containing anti-blocking agent, about 5% by weight of amide waxes, and about 1% of a lubricating agent. The amide waxes and lubricating agent are well known in the art as slip agents.

The ethylene propylene terpolymer was blended with the propylene in a blend ratio of about 92% by weight EPC and 8% by weight PP. (The PP percentage includes the additives discussed above).

A circular coextrusion die was fed with three extruders to prepare a five layer shrink film. One extruder was used to feed the blend of EPT and polypropylene as a melt to the extrusion die to form the outer layers. Another extruder fed an ethylene propylene copolymer-based anhydride-modified adhesive (Admer QF 551A) available from Mitsui to the extrusion die to provide the adhesive as intermediate layers in the multilayer film. The third extruder provided molten EVOH (EVAL EP H103B from EVALCA) to the extrusion die. This particular EVOH has an ethylene content of about 38%.

The extruded tape was rapidly cooled to room temperature and collapsed by pinch rolls. The tape was subsequently heated to its orientation temperature, in the range of 105°C to 115°C. Using a bubble technique well known in the art, internal air pressure stretched the tape to about 3.5 times its unstretched dimensions in both the longitudinal (machine) and transverse directions to form a bubble which provides biaxial orientation to the resulting film. The bubble was then rapidly cooled by chilled air in order to maintain the oriented state of the film. Finally, the bubble was collapsed and the expanded film gathered on a take-up roll. After orientation, the total wall thickness of the film was about one mil with 60% of the structure being the blend of ethylene propylene terpolymer and polypropylene; 25% of the structure being the anhydride-modified adhesive layers; and the remainder or 15% of the structure being the core barrier layer.

It will be clear to one skilled in the art that the degree of stretching may be varied to obtain the desired degree of film gauge or thickness and to regulate the desired amount of shrink tension, free shrink, and other shrink properties of the final film, depending on the packaging application. Preferred stretching or racking ratios are between about 3.0 and 4.0 in both the machine and transverse directions.

In this example, the film showed tensile strengths at break of 15,240 psi in the longitudinal direction and 14,340 psi in the transverse direction (ASTM D882-81 at 73°F). The film showed a modulus of 161,000 and 157,600 in the longitudinal and transverse directions respectively (ASTM D882-81 at 73°F).

The film exhibited a free shrink ranging from 20% in a longitudinal direction (24% transverse direction) at 220°F to 48% longitudinal direction (48% transverse direction) at 260°F (ASTM D2732-70). Shrink tension varied from 406 psi longitudinal (470 psi transverse) at 220°F up to 483 psi longitudinal (533 psi transverse) at 260°F (ASTM D2838-81).

The film also exhibited good optical properties including haze (5.1% at 73°F) (ASTM D1003-61); clarity (41% at 73°F) (ASTM D 1746-70) and gloss (75 at 73°F) (ASTM D2457-70).

This film was also characterized by excellent oxygen barrier characteristics, having an oxygen transmission at 73°F, 0% relative humidity of 3 CC STP/(24 hours, square meter atmosphere) (ASTM D3985-81).

EXAMPLE 2

A second multilayer shrink film is made by the same method described above except that the ethylene propylene terpolymer comprises substantially all of the outer layer.

The films of the present invention provide heat sealable outer layers, and the orientation of the film provides toughness and improves the resistance to oxygen permeability.

An important feature of the film is its thinness. The multilayer film is preferably 0.5 to 4 mils thick, and more preferably 0.5 to 2 mils thick. One mil is equal to one thousands of an inch. It has been found that, when using a blown bubble orientation process, orienting the multilayer films of the present invention is increasingly difficult for

thicknesses greater than about 2 mils, and very difficult or impractical for thicknesses greater than about 4 mils. Thicknesses greater than about 4 mils can be more readily achieved by alternative orientation processes such as the tenter frame process well known in the art.

The blend ratios of the EPT and PP may be varied according to desired properties or end-use of the multilayer film. For example, increasing the polypropylene in the blend will add stiffness to the film, but also increase the sealing temperature of the film. Conversely, increasing the EPT in the blend tends to lower the shrink temperature of the oriented film, or to increase shrink at the same temperature, and also lowers the sealing temperature of the film. A preferred blend includes between about 4% and 15% PP and between about 96% and 85% EPT.

The multilayer film of the present invention is oriented either monoaxially or biaxially, and preferably used as a shrink film. Optionally, the oriented film may be further processed by reheating the film to a temperature near its orientation temperature, i.e. either somewhat below, at, or somewhat about its orientation temperature, to heat set the film. This future processing step has the advantage of substantially retaining many of the favorable physical characteristics of an oriented film, such as higher modulus and improved optical properties, while providing a substantial shrink-free film in applications where a shrink feature is undesirable.

Obvious modifications to the invention as described may be made by one skilled in the art without departing from the spirit and scope of the claims as presented below. For example, although the film has been described primarily as a coextruded film, other processes well known in the art, such as conventional lamination and extrusion coating, can also be used to produce films of the present invention.

CLAIMS

1. A polymeric film comprising:

- a core layer comprising ethylene vinyl alcohol copolymer; and
- two outer layers comprising ethylene propylene terpolymer.

2. A film according to claim 1 further comprising an intermediate layer, on opposite surfaces of the core layer, comprising a polymeric adhesive which bonds the core layer to each respective outer layer.

3. A film according to claim 2 wherein the adhesive is a carboxylic acid or acid anhydride-modified polyolefin.

4. A film according to claim 3 wherein the adhesive is a polypropylene-based carboxylic acid or acid anhydride-modified polyolefin.

5. A film according to any one of the preceding claims wherein the outer layers each comprise a blend of between 0% and 100% ethylene propylene terpolymer and between 100% and 0% polypropylene.

6. A film according to any one of the preceding claims wherein polypropylene comprises between about 4 and 15% by weight of the outer layers.

7. A film according to any one of the preceding claims wherein polypropylene comprises about 8% by weight of the outer layers.

8. A film according to any one of the preceding claims wherein the film has been oriented by racking at a racking ratio of from about 3.0 to about 4.0 in both the longitudinal and transverse directions.

9. A film according to any one of the preceding claims wherein the film has been oriented by racking at a racking ratio of about 3.5 in both the longitudinal and transverse directions.

10. A film according to any one of the preceding claims having longitudinal and transverse free shrink of at least 17% at 200°F.

11. A film according to any one of the preceding claims wherein the total film thickness is from about 0.5 to 4 mils.

12. A film according to any one of the preceding claims wherein the total film thickness is from about 0.5 to 2 mils.

13. A film according to claim 1 substantially as hereinbefore described in Example 1 or 2.

14. A method for the manufacture of a polymeric film according to any one of the preceding claims comprising the steps of:

(a) coextruding a core layer of ethylene vinyl alcohol copolymer, two outer layers comprising ethylene propylene terpolymer and polypropylene and, optionally two intermediate layers of

adhesive;

(b) rapidly cooling the coextruded multilayer film;

(c) collapsing the cooled film;

(d) heating the collapsed film to its orientation temperature; and

(e) stretching and orienting the heated film.

15. A method according to claim 14 wherein the coextruded multilayer film is cooled to about room temperature.

16. A method according to claim 14 or 15 wherein the heated film of step (d) is stretched at a racking ratio of from about 3.0 to about 4.0 in both the longitudinal and transverse directions.

17. A method according to claim 14, 15 or 16 wherein the heated film of step (d) is stretched at a racking ratio of about 3.5 in both the longitudinal and transverse directions.

18. A method according to any one of claims 14 to 17 further comprising the step of reheating the oriented film to a temperature near its orientation temperature.

19. A method for the manufacture of a polymeric film according to claim 14 substantially as hereinbefore described in Example 1 or 2.

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